INVESTIGATION ON THE REACTIVITY OF CALCIUM MINERALS UNDER SIMULATED VENUS CONDITIONS.

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Introduction

- Venus' atmosphere has trace abundances (120-180 ppmv) of SO_2
- SO_2
  - SO_2 gas is present in volcanic environments on Earth
  - Its interactions with minerals have been investigated in conditions present near volcanic vents and eruption plumes (Renggli et al. 2019; Delmelle et al., 2018; Prinn and Fegley, 1989)
  - SO_2 is reactive with several common elements including calcium; common outcome is $CaSO_4$ (anhydrite)
  - The kinetics of these reactions are not well documented, and very little investigations have been completed at Venus conditions

Introduction

- Knowledge on chemical reactions has implications for the past and current state of Venus
  - Venus may have had liquid water on its surface, thus hydrous silicates may have formed at that time
  - To determine if these minerals are still present, tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) and phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$) were tested at simulated Venus conditions (Johnson and Fegley, 2003; 2003; 2005)
    - Conclusion:
      - They break down over billions of years and may still be present
      - However, experiments were not completed in SO_2

Introduction

- The Venus Emissivity Mapper (on VERITAS and EnVision) will be used to determine the presence and relative abundance of transition metals (mostly FeO) in the surface rock
  - Calcium diffuses through basalt to react with CO_2 and SO_2, changing the observed bulk composition and could potentially decrease the emissivity from orbit (Dyar et al., 2021)
  - Experiments investigating kinetics will be informative for future emissivity data

Objectives

- Investigate the interactions between several calcium bearing minerals and SO_2
  - Constrain the reaction rate
  - Determine the effect of crystal lattices

Methods

- Sample:
  - Cut with diamond saw
  - Polished to 0.5 μm
  - Cleaned in an ultrasonic bath
  - Wrapped with gold wire
  - Weighed

Mineral	Chemical Composition
Calcite	$CaCO_3$
Wollastonite	$CaSiO_3$
Anorthite	$CaAl_2Si_2O_8$
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
Grossular	$Ca_3Al_2(SiO_4)_3$

Methods

- Experiment
  - Sample is hung in the center of ceramic tube in TGA (Thermogravimetric Analysis)
  - Tested Temperatures:
    - 460°C: average lowland temperature on Venus
    - 700°C: to decrease experiment time
  - Tested Gas:
    - CO_2/1.5% SO_2: SO_2 abundance similar to molecular number density as on Venus
    - 99.99% CO_2
  - Temperature and mass of sample are collected in real-time

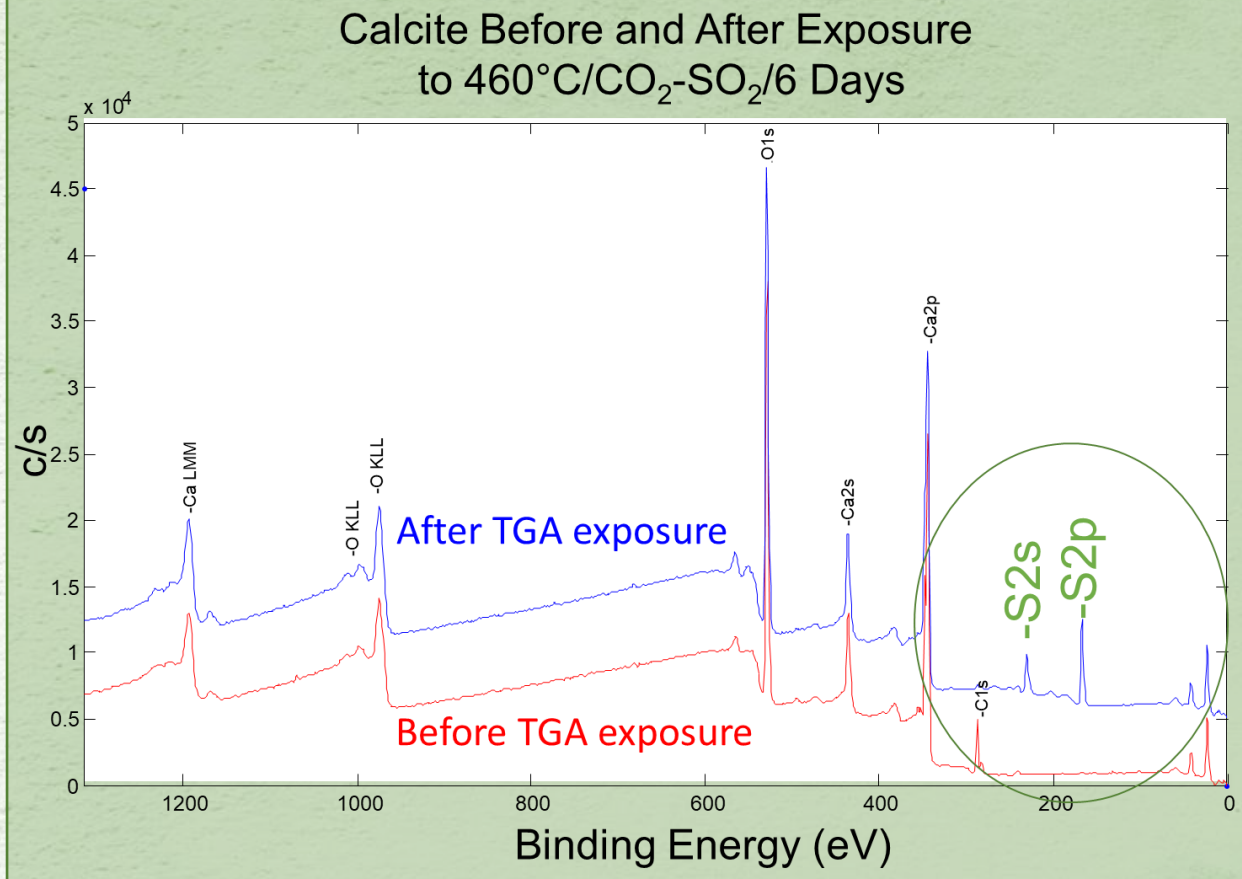
Methods

- Analysis
  - Mineralogy confirmed with X-Ray Diffraction (XRD)
  - Surface chemistry analysis with X-ray Photoelectron Spectroscopy (XPS)
  - Mill using a Focused Ion Beam (FIB)
  - Analyze with Scanning Electron Microscope/Energy Dispersive X-Ray Spectroscopy (SEM/EDS)

Results

Mineral	Temp	Gas	Time
Calcite	460°C	CO_2/SO_2	6 days
Calcite	700°C	CO_2	5 days
Calcite	700°C	CO_2/SO_2	5 days
Wollastonite	460°C	CO_2/SO_2	6 days
Tremolite	460°C	CO_2/SO_2	6 days
Anorthite	460°C	CO_2/SO_2	6 days

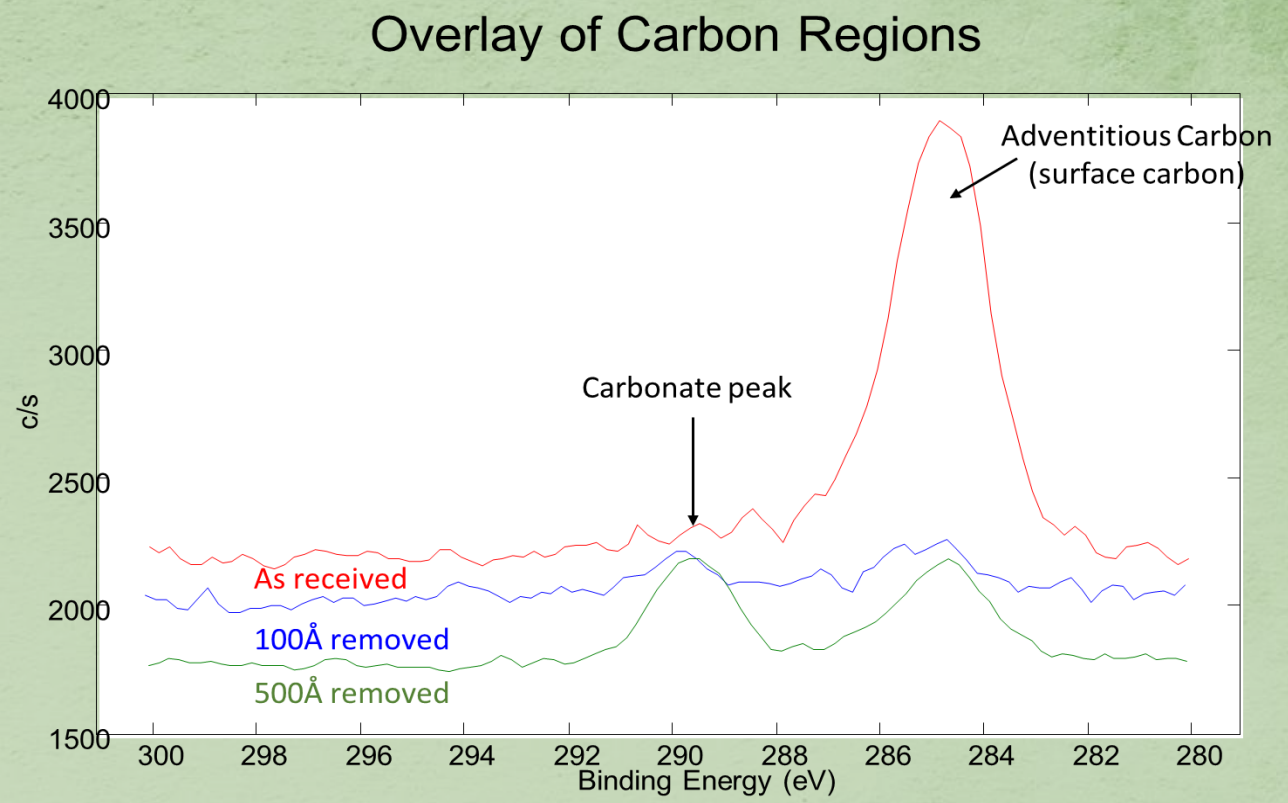
Results: Calcite heated to 460°C in CO_2/SO_2 for 6 days



	at %	
	Ca	**S**
Surface	11.5	0.8
sputtered 1 min (100 Å)	20	nd
After Experiment		
Surface	14.4	15.1
sputtered 1 min (100Å)	18.2	14.1
sputtered 5 min (500Å)	20.8	10.6

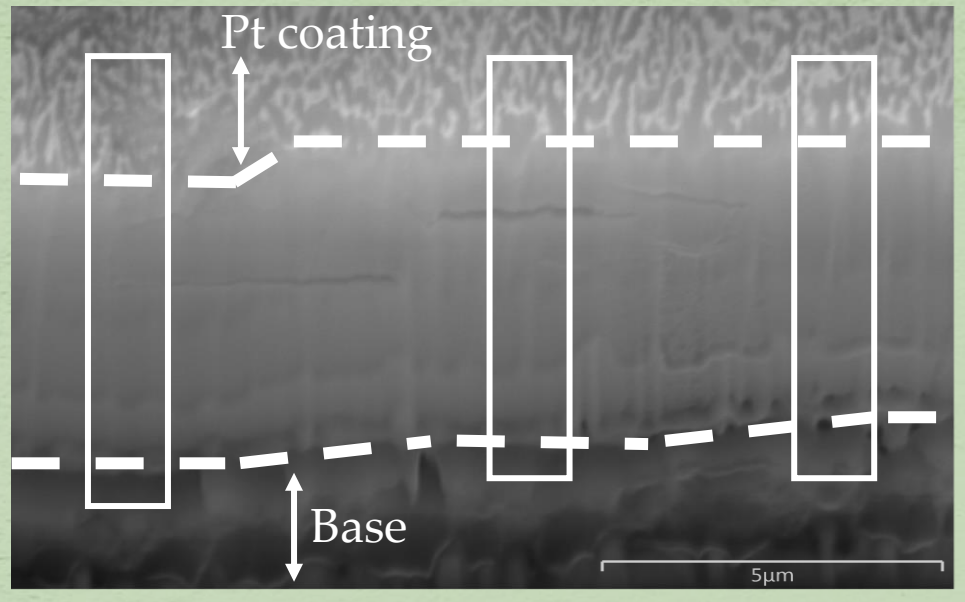
Sulfate ($[SO_4]^{2-}$) is present after the experiment

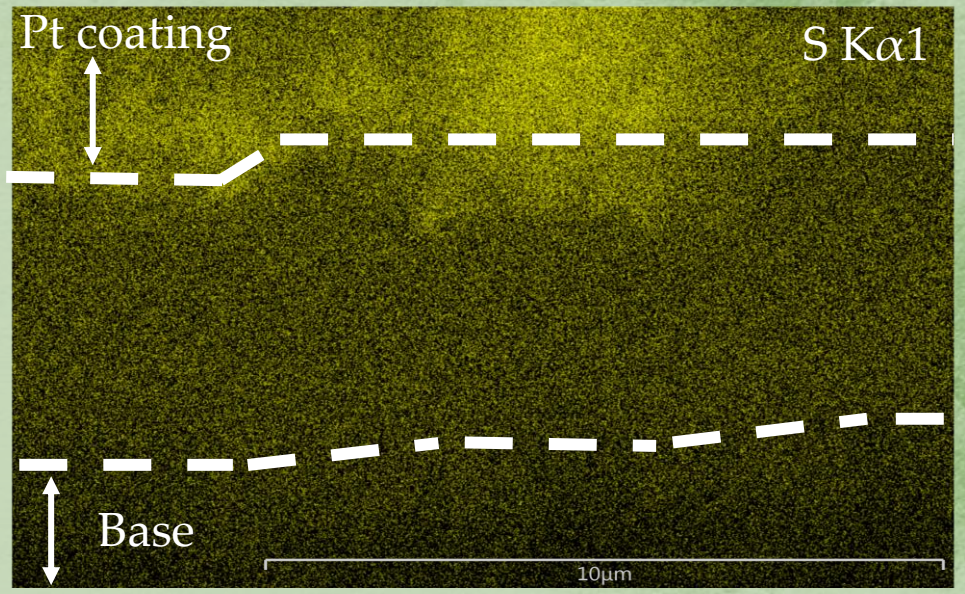
Results: Calcite heated to 460°C in CO_2/SO_2 for 6 days



Absence of carbonate peak ($[CO_3]^{2-}$) at the surface after the experiment

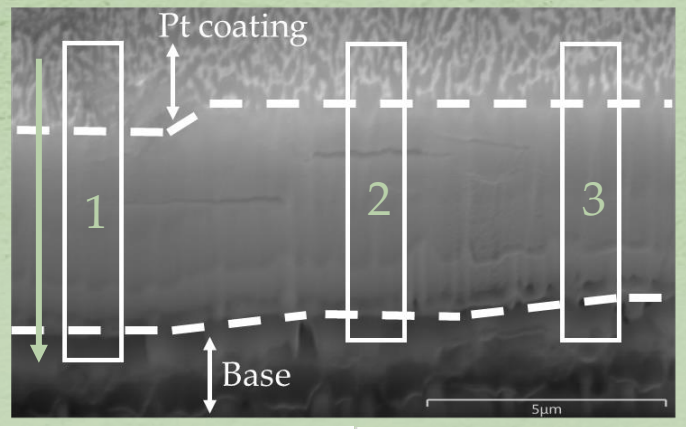
Results: Calcite heated to 460°C in CO_2/SO_2 for 6 days

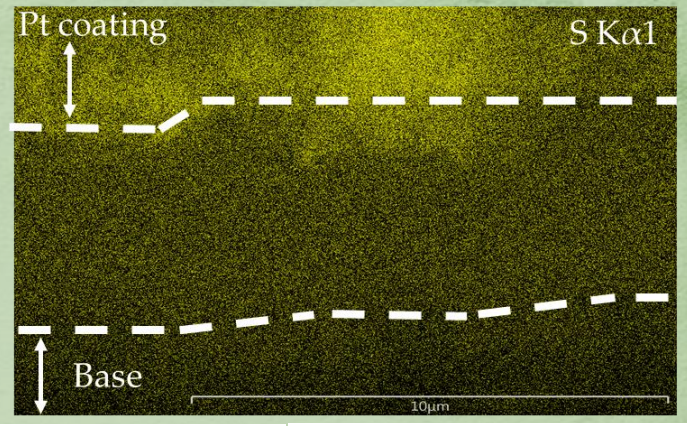


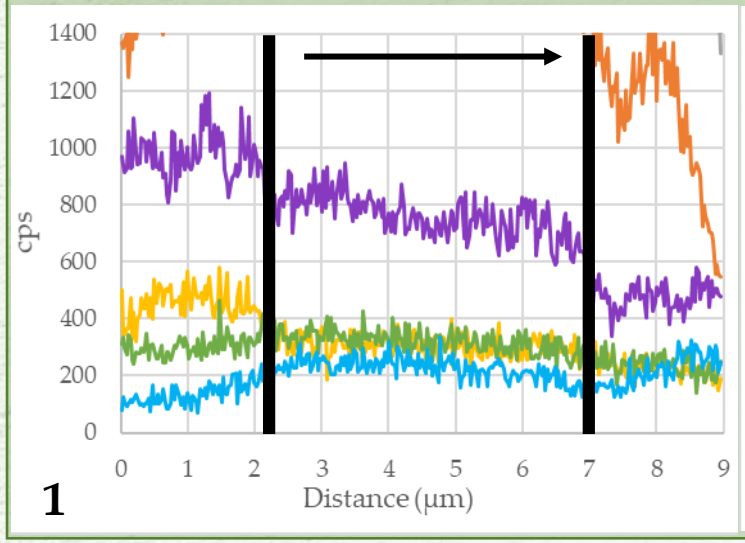


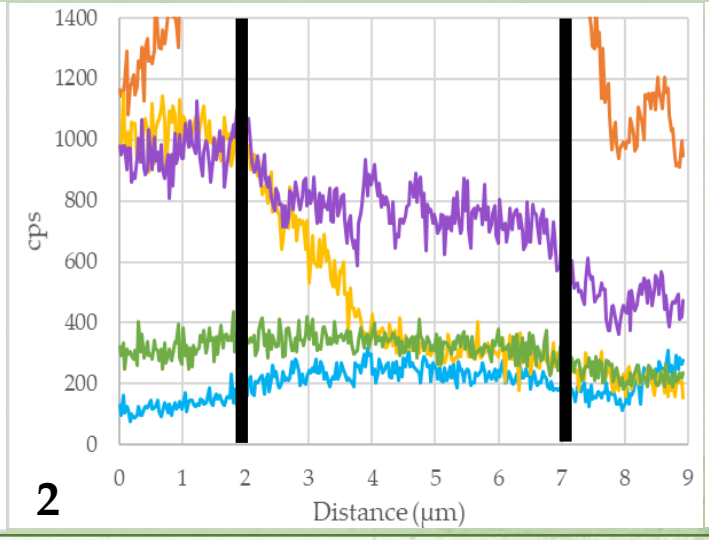
Sulfur is present at the top of the sample and part of the top of the cliff wall

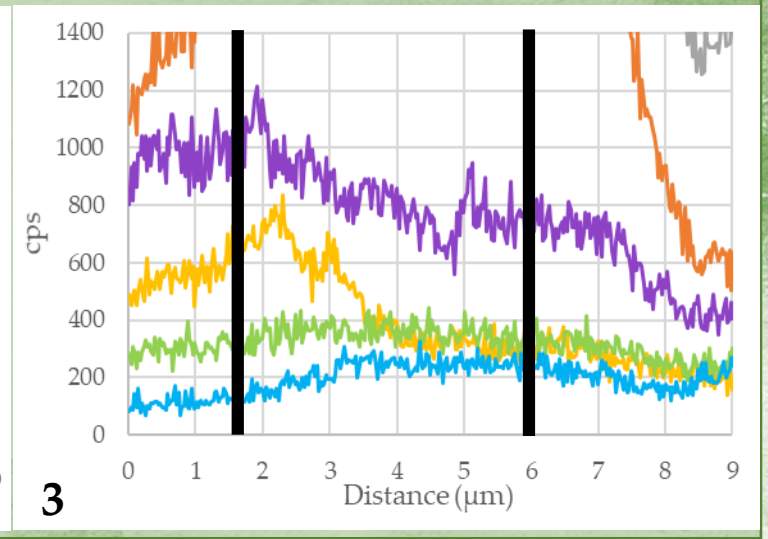
Results: Calcite heated to 460°C in CO_2/SO_2 for 6 days



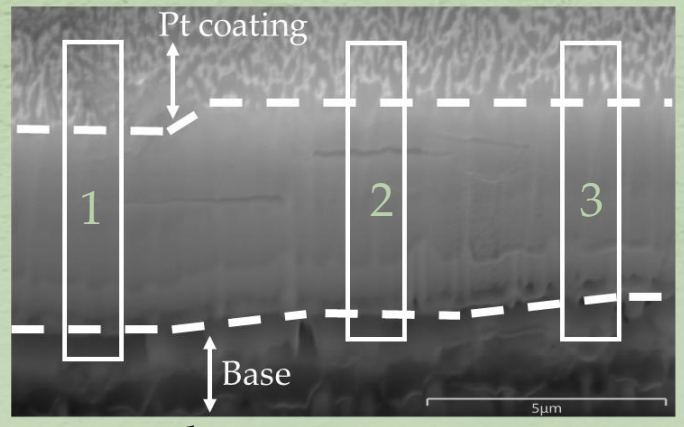


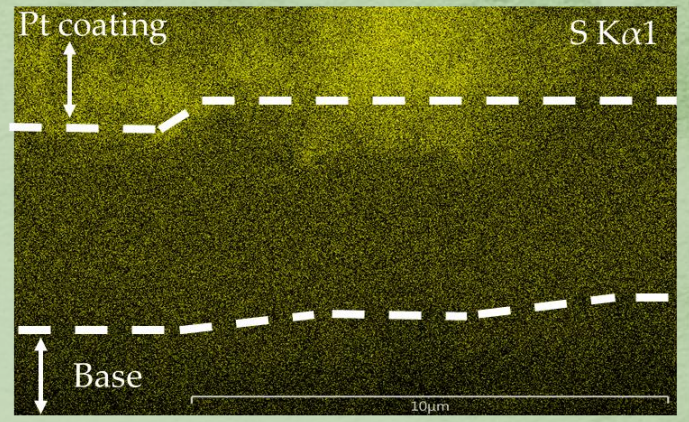


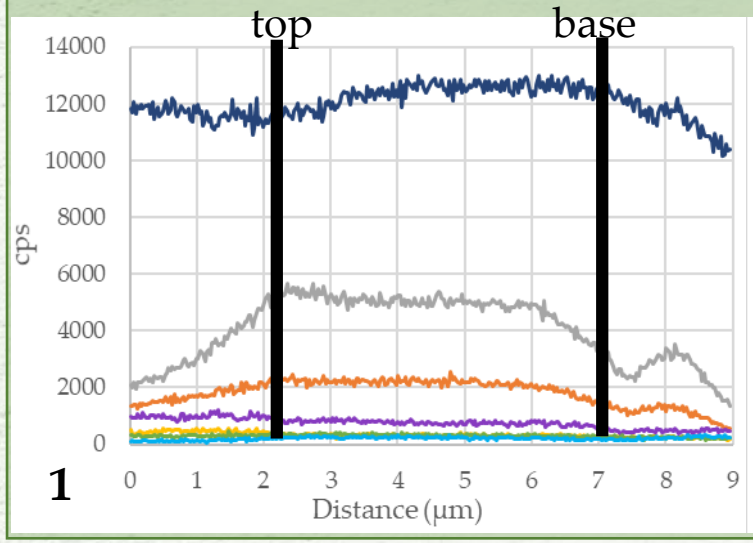


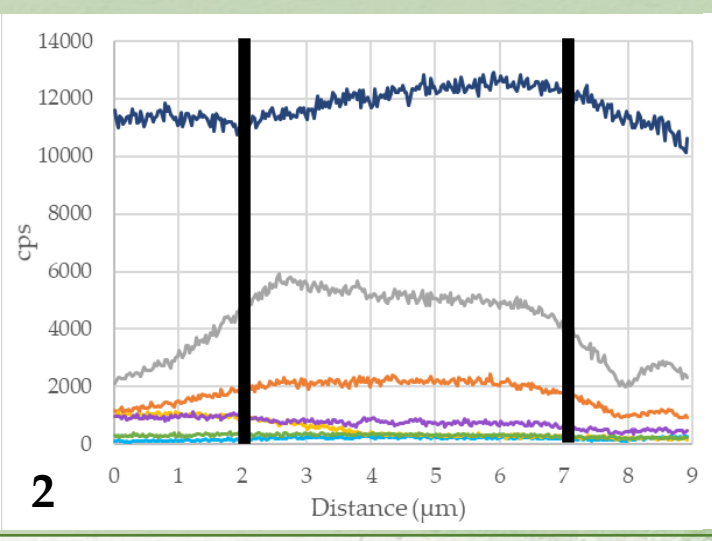


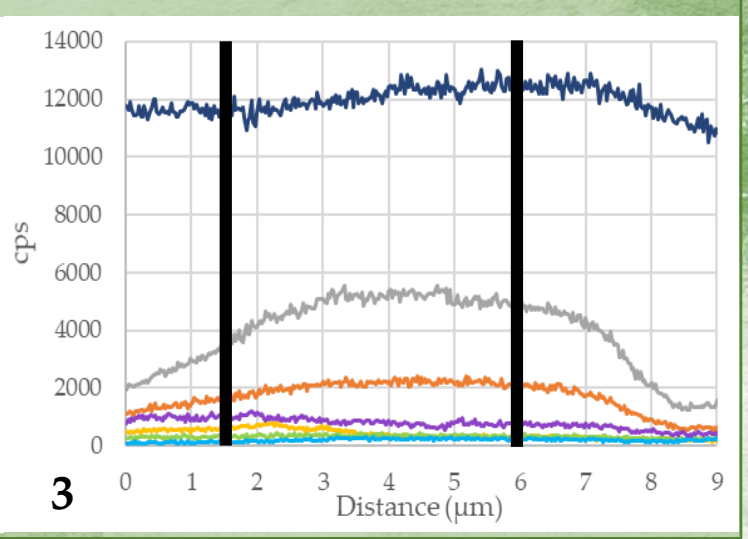
Results: Calcite heated to 460°C in CO_2/SO_2 for 6 days



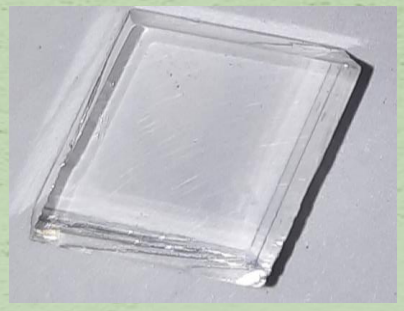




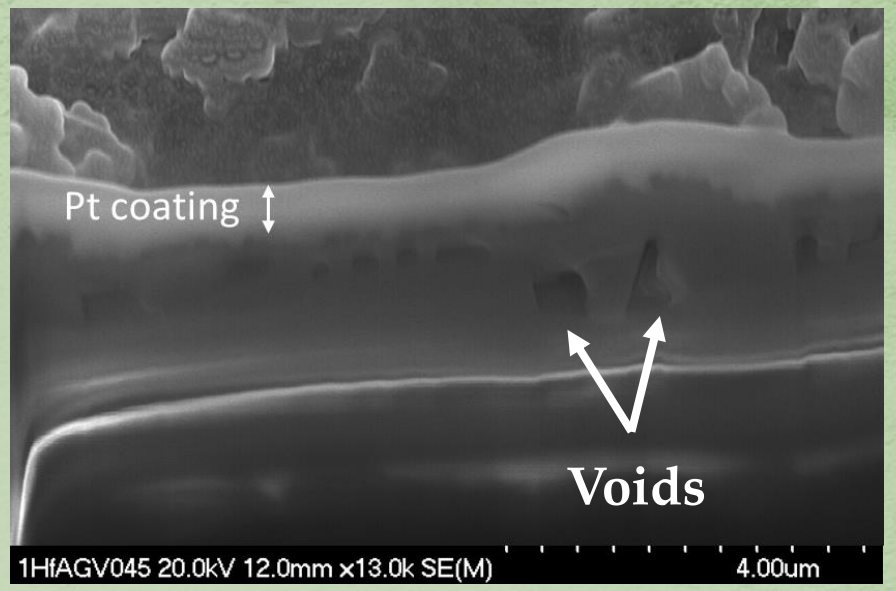




Results: Calcite heated to 700°C in CO_2/SO_2 for 5 days

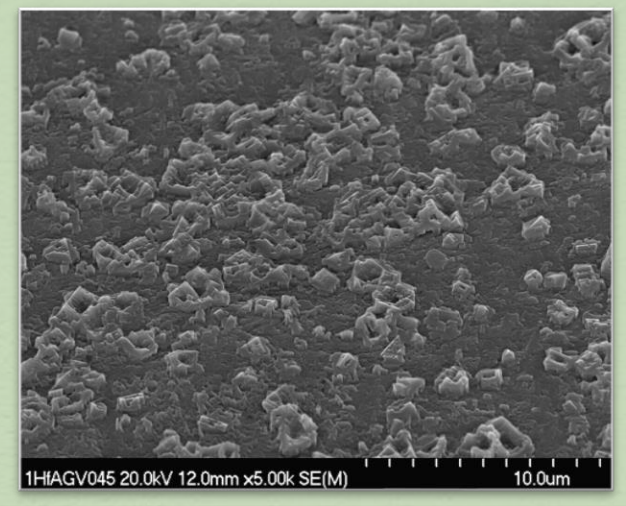


Calcite before (left) and after (right) it was heated



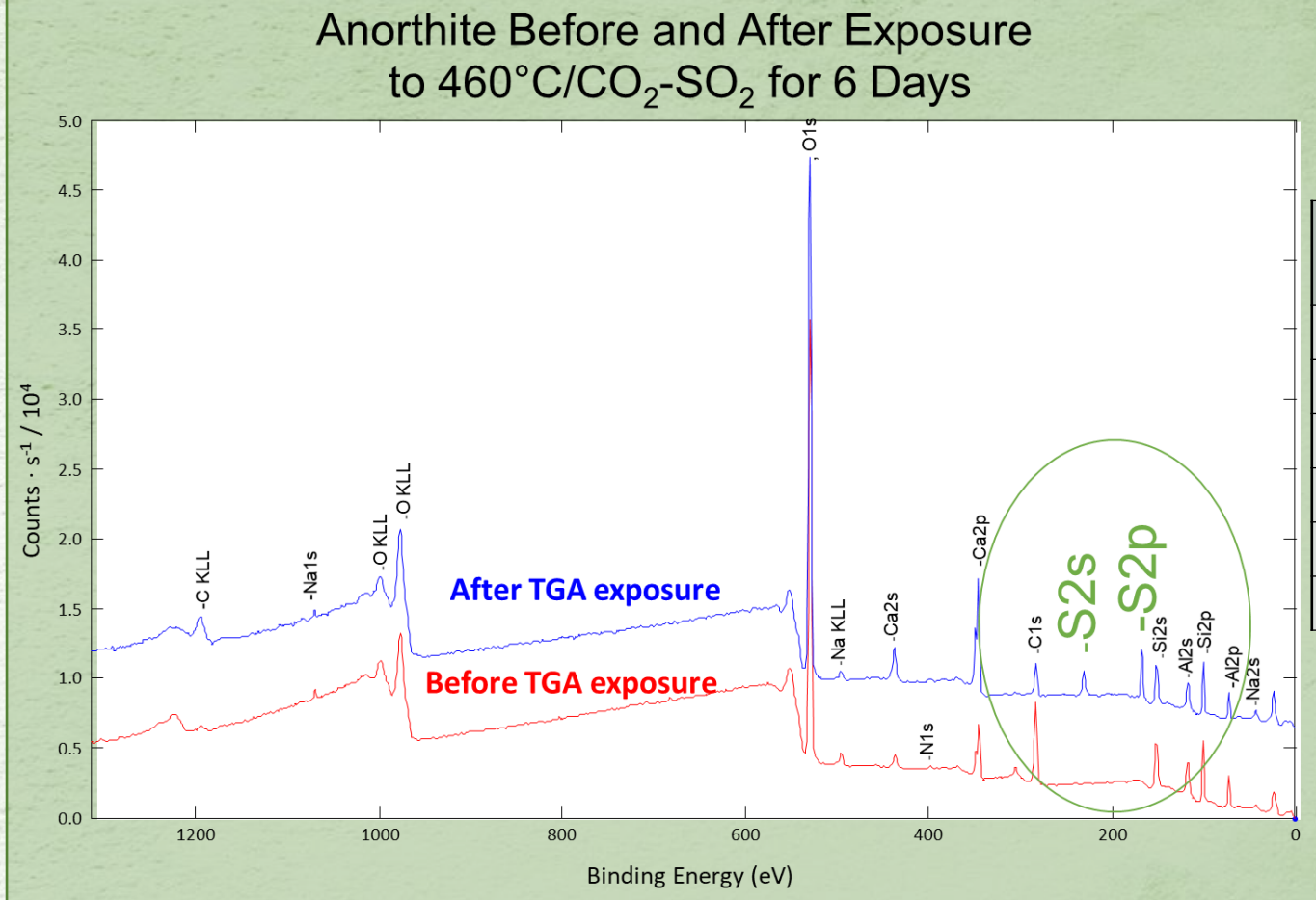
The cliff face of the sample after it was milled via FIB. Void spaces are visible in the wall.

The surface of calcite after the experiment



Calcite heated in pure CO_2 did not have voids nor secondary crystal structures on the surface. Both formations are likely correlated to SO_2.

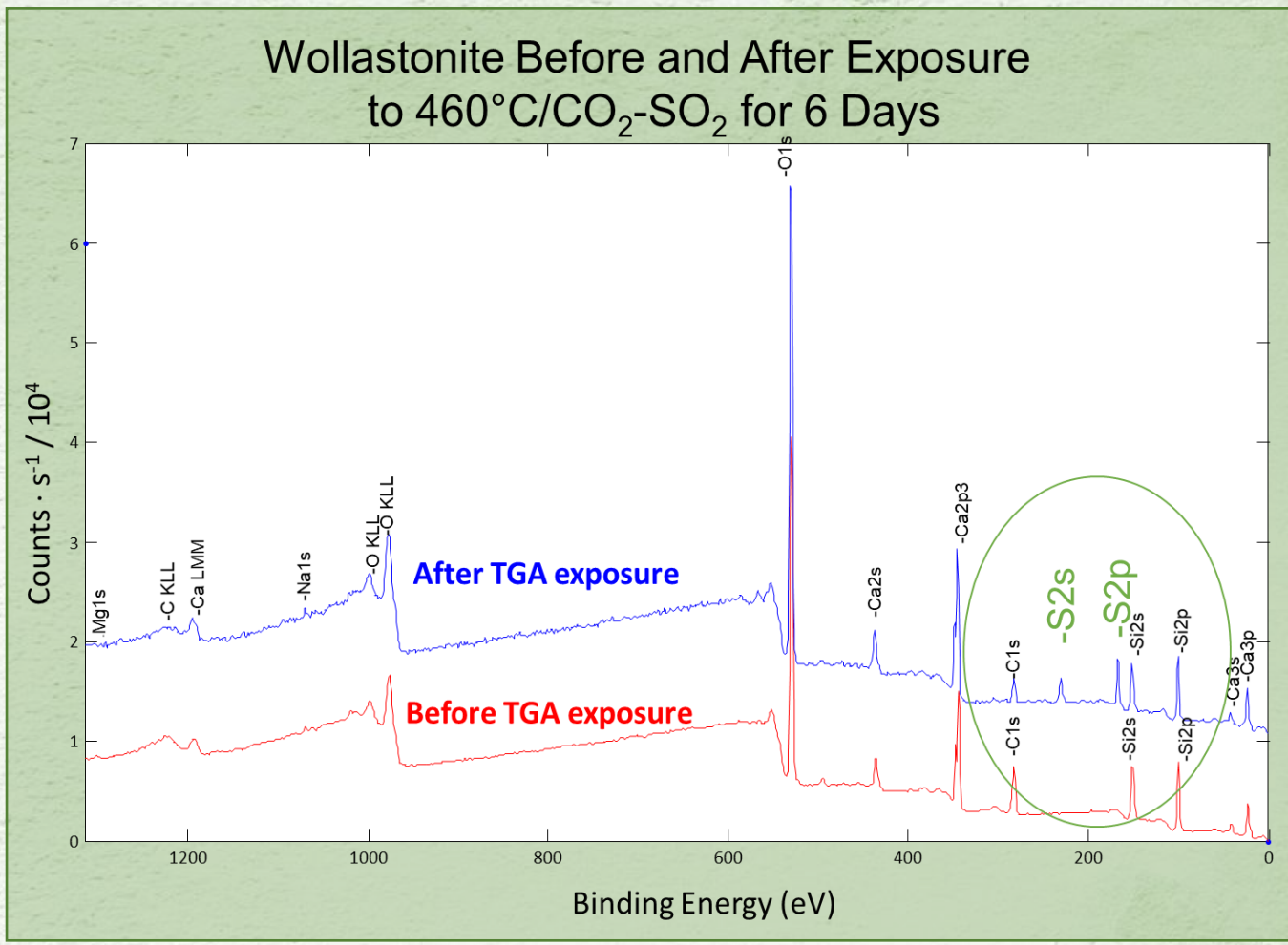
Results: Anorthite heated to 460°C in CO_2/SO_2 for 6 days



	at %	
	Ca	**S**
Surface	2.7	nd
sputtered 1 min (100 Å)	4.3	nd
After Experiment		
Surface	6.2	5.9
sputtered 1 min (100Å)	5.8	0.2

Sulfate is present after the experiment, but surficial. Crystal structure inhibits reaction.

Results: Wollastonite heated to 460°C in CO_2/SO_2 for 6 days



	at %	
	Ca	S
Surface	6.8	nd
sputtered 1 min (100 Å)	8.7	nd
After Experiment		
Surface	8.5	6.1
sputtered 1 min (100Å)	10.9	2.5
sputtered 2 min (200 Å)	11.8	1.6

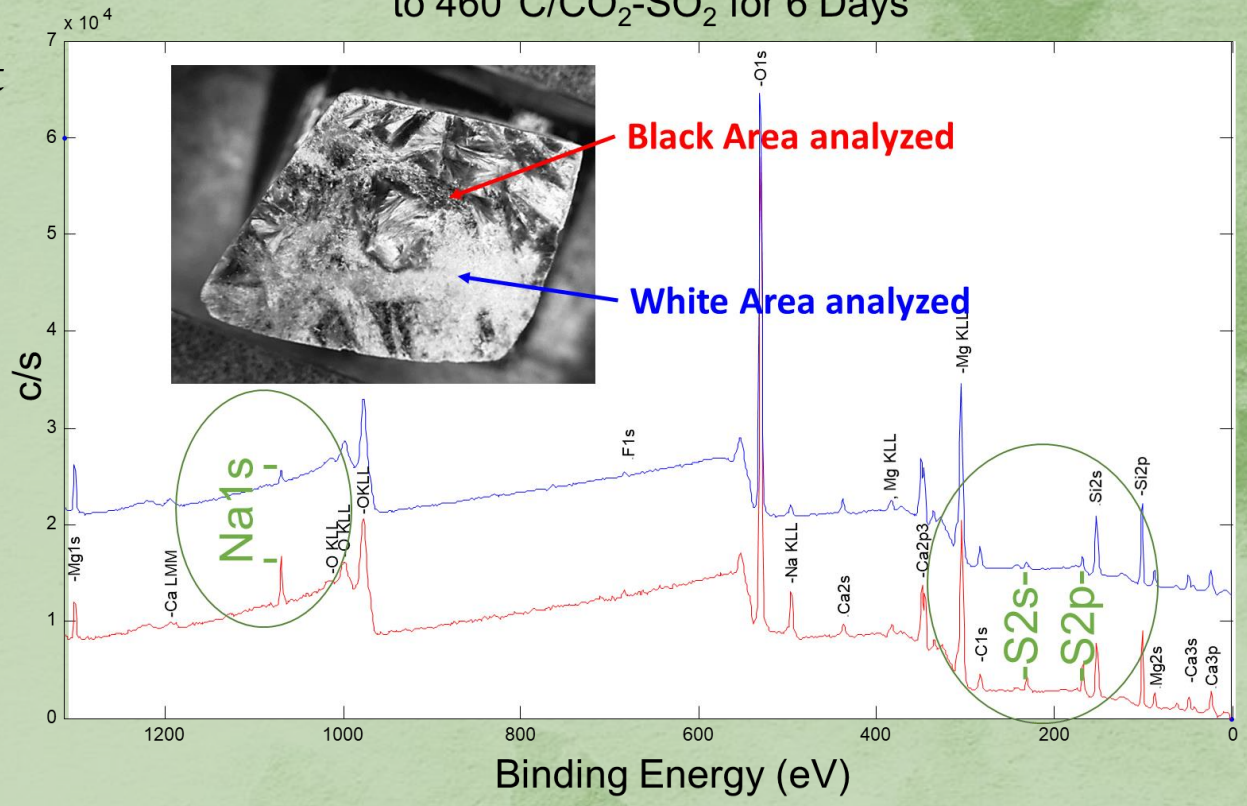
Sulfate is present after the experiment

Results: Tremolite heated to 460°C in CO_2/SO_2 for 6 days

Tremolite before (left) and after (right) the experiment

	at %		
	Ca	**Na**	**S**
Surface	1.5	0.4	nd
sputtered 1 min (100 Å)	2.5	nd	nd
After Experiment			
Surface Black Area	3.3	4.1	4.1
sputtered 1 min (100Å)	4.3	4.3	1.4
sputtered 2 min (200Å)	3.8	4.1	1.1
Surface White Area	3.6	1.7	2.6

Black and White Crystals of Tremolite After Exposure to 460°C/CO_2-SO_2 for 6 Days



Results

This ratio provides insight into the depth of S in the sample, its potential relationship to Ca, and may be used to complement the EDS data on the cliff wall.

Mineral	Location	S/Ca ratio	S (at %)
Calcite	Surface	1.05	15.1
	Sputtered 1 min (100Å)	0.77	14.1
	Sputtered 5 min (500Å)	0.51	10.6
Wollastonite	Surface	0.72	6.1
	Sputtered 1 min (100Å)	0.23	2.5
	Sputtered 2 min (200 Å)	0.14	1.6
Anorthite	Surface	0.95	5.9
	Sputtered 1 min (100Å)	0.03	0.2
Tremolite	Surface (dark grey)	1.24	4.1
	Sputtered 1 min (100Å) (dark grey)	0.33	1.4
	Sputtered 2 min (200 Å) (dark grey)	0.29	1.1
	Surface (white)	0.72	2.6

Anhydrite, $CaSO_4$, Ca:S is 1:1

Summary

- All samples formed sulfate on the surface
- Calcite is reactive with SO_2 and will produce $CaSO_4$ at the surface, but the reaction is slower at 460°C compared to 700°C
- According to XPS results, wollastonite, anorthite, and tremolite are less reactive to SO_2 than calcite (460°C in CO_2 -1.5% SO_2 for 6 days)
- Higher abundance of calcium at the surface after an experiment
- Longer experiments will be completed in the future
- This information combined with the dimensions of the sample and the known change in mass will be used to constrain the reaction rate

Acknowledgements

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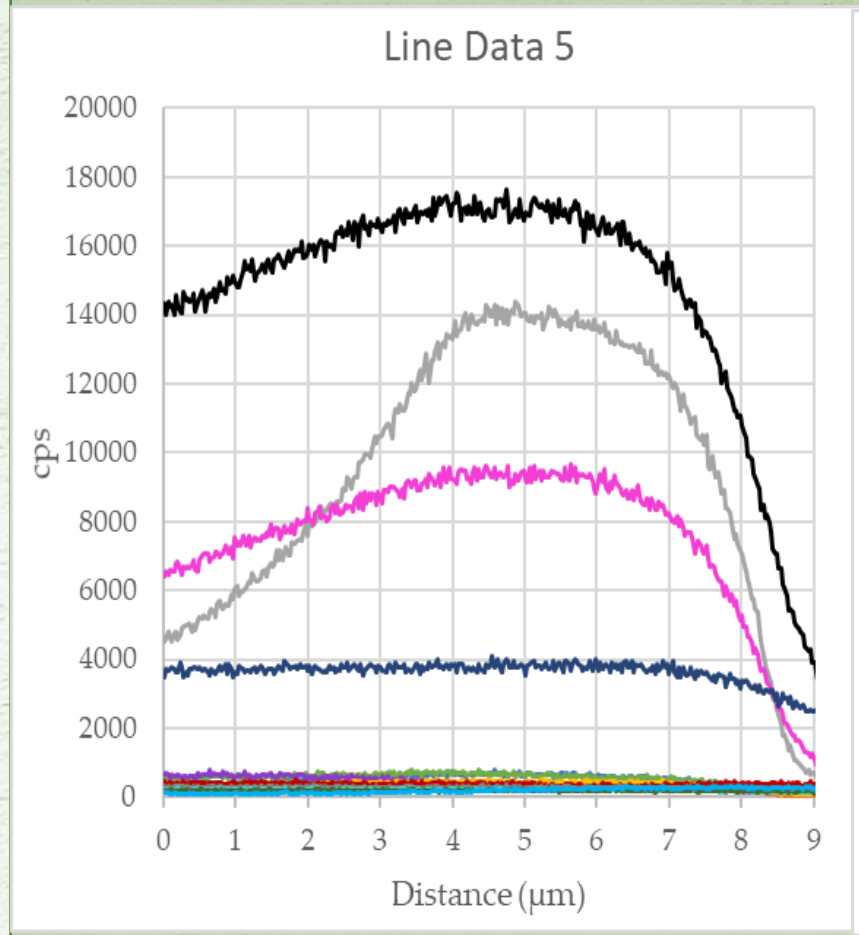
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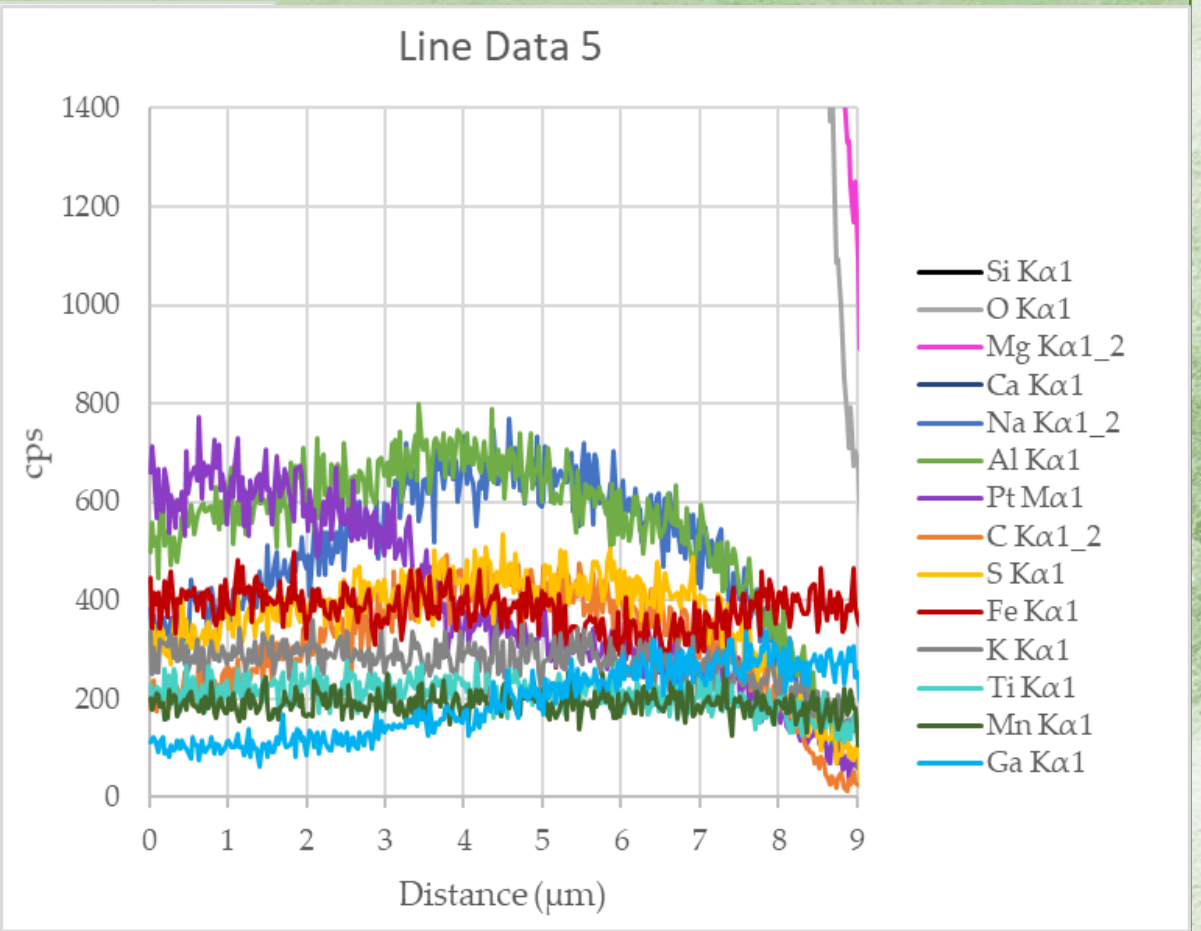
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Distance (µm)
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200
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1400
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O Kα1
Mg Kα1_2
Ca Kα1
Na Kα1_2
Al Kα1
Pt Mα1
C Kα1_2
S Kα1
Fe Kα1
K Kα1
Ti Kα1
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